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ORGANIC AZIDES AS JET FUEL ADDITIVES(U) NORTHWESTERN
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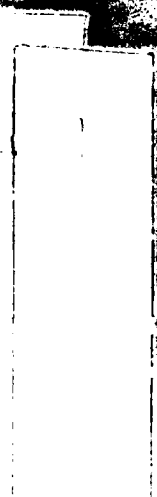
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FINAL REPORT

ORGANIC AZIDES AS JET FUEL ADDITIVES

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(M.K. Ellingsworth, Program Director)

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SUMMARY

Under the sponsored program an experimental investigation has been conducted on the vaporization and combustion characteristics of freely-falling droplets of organic azides in hot oxidizing or inert environments. The droplet burning rate and the state of micro-explosion have been measured. Results show that, compared with the conventional hydrocarbon fuels, droplets of azido fuels burn faster and micro-explode earlier in the droplet lifetime. The effect is especially strong for diazido n-alkanes whose gasification rates can be several hundred percent of the corresponding n-alkanes. Such strong responses are postulated to be caused by dissociative gasification with very low heat of gasification.

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INTRODUCTION

In most liquid-fueled combustors such as the ramjet, the fuel is directly introduced into the upstream flow section of the combustion chamber in the form of sprays of droplets. These droplets subsequently mix with the external gas, heat up, gasify, combust, and thereby release heat to provide the propulsion energy. It is therefore obvious that the rates of gasification and mixing would closely affect the chemical heat release rate and consequently such important performance parameters as combustion efficiency and the tendency to exhibit combustion instability.

In order to achieve a controlled, high heat release rate, we first note that the rate of droplet gasification basically follows the classical d^2 -Law,¹ that is the square of the droplet diameter decreases linearly with time. This implies that the lifetime of a droplet should vary approximately quadratically with its initial diameter. This, of course, forms the basis of the spraying/atomization principle as means of rapidly gasifying a given mass of liquid.

Attempts at enhancing the overall droplet gasification rate, and thereby reducing the combustor size, have emphasized the production of small droplets through spraying as well as increasing the gasification rates of individual droplets. Both approaches, however, have inherent difficulties. Concerning atomization, we note that there are three factors which place lower limits on the attainable initial droplet size. The first is that, physically, droplets of infinitesimally small sizes cannot be produced through spraying. Secondly, exceedingly small droplets also lack sufficient inertia for penetration and therefore are undesirable from consideration of macro-scale mixing and homogeneity. Thus relying on spraying alone frequently cannot yield optimum gasification rate and mixture homogeneity. The third factor is that recent studies² on the behavior of dense sprays have shown that even if very small droplets can indeed be produced, they will nevertheless collide and coalesce into much bigger droplets in the dense spray region next to the nozzle.

Concerning the droplet gasification rate, it is also well established that, for conventional hydrocarbon fuels, this rate is quite insensitive to changes in the system parameters in that while increases of tens of percents can be achieved through, say, convective augmentation or oxygen enrichment, increases by a factor of two or more are difficult to attain.

In view of the difficulty in manipulating the droplet gasification rate by changes in the atomization processes and environment parameters, an alternate approach is to modify the fuel structures and/or composition. A promising candidate as either jet fuel or jet fuel additive is the family of organic azides.³ Structurally, an azide functional group consists of three linear nitrogen atoms linked by resonating multiple bonds. In an organic azide, one or more of these azide groups is attached to an organic molecule; thus we can have, for example, mono-azides ($R'-N_3$), di-azides ($N_3-R''-N_3$), and etc. For obvious reasons we are only interested in organic compounds which are exothermic when oxidized. The potential of the azides is that they decompose upon heating, releasing heat and nitrogen which could significantly enhance the overall droplet gasification rate. Typically, the decomposition involves cleavage of the center nitrogen



to yield a highly reactive nitrene intermediate and molecular nitrogen.

The nitrene radical undergoes rapid rearrangement and reaction with neighboring molecules and can yield a large number of stable decomposition products depending on the size and complexity of the R group. Pritzkow and Timm⁴ conducted gas-phase pyrolysis of several alkyl azides and found that a majority of the nitrenes either rearranged themselves to form various imines and heterocyclic compounds, or combined with neighboring molecules to form primary and secondary amines. Although it is likely that some of the recombination reactions may be endothermic, the overall decomposition is highly exothermic. From thermal-explosion induction times, Rice and Campbell⁵ were able to estimate a heat of decomposition of 55 kcal/mole for azidoethane, which is significant as compared to the additional heat release of 350 kcal/mole from the oxidation of the decomposed products.

Thus if decomposition occurs in the gas phase, after the azides are gasified, then the relative ease of decomposition together with its heat release are expected to facilitate ignition and flame propagation when premixed burning occurs in the bulk medium. The droplet gasification rate, however, is not expected to be much affected because the decomposition takes place away from the droplet.

On the other hand if decomposition occurs in the liquid phase, within the droplet interior, then the intense internal pressure build-up due to gas generation is expected to totally pulverize the droplet and thereby cause almost instantaneous droplet gasification. The reduction in the total gasification time can be significant. Indeed, this micro-explosive phenomenon has been previously studied for other fuel systems such as water/oil emulsions, coal-oil mixtures, and miscible fuel blends.⁶⁻⁸

The objective of the present investigation is to experimentally explore and quantify the burning characteristics of freely-falling single droplets of organic azides and their mixtures with other hydrocarbon fuels in combustion environments of given temperature and oxygen concentration. The experimental methodology is discussed in the next section, which is then followed by presentation and discussion of the experimental results. It will be shown that the gasification times of certain organic azides are indeed very short, thereby offering substantial promise for further development.

EXPERIMENTAL METHODOLOGY

The experiment involves the combustion of freely-falling droplets in the postcombustion zone of a flat-flame burner. The droplets are generated by the ink-jet printing technique which yields a stream of monodisperse droplets of controlled size, spacing, and velocity. The temperature and composition of the combustion products from the flat-flame burner can be manipulated by varying the composition of the premixed gas consisting of methane, oxygen, and air. Thus the combustion environment of the droplets can be controlled.

The droplet image was photographically determined using strobe lighting synchronized with the ink-jet pulse generator. Temporal variation of the image was controlled by a delay circuit. The extremely

short flash duration of the strobe light essentially freezes the droplet motion, as is clear from the photographs of the droplets to be discussed subsequently. It may also be mentioned that in the present experiments both the gas as well as the droplet streams are very steady. The droplet location does not wander more than one-quarter of the droplet diameter early in the lifetime, and one droplet diameter in the later stages. This assures the high accuracy and reliability of the data obtained.

In the present experiments the initial droplet diameter was varied from 250 to 350 μm , the initial droplet velocity is about 80 cm/s, and the droplet spacing is in excess of 100 droplet diameters so that there is practically no droplet-droplet interaction. The droplet Reynolds number is estimated to be always less than one.

In the case of droplet combustion the oxygen concentration was at 21 mole % while the gas temperature was at 1150 K. For pure vaporization the oxygen concentration was essentially zero while the gas temperature was again at about 1150 K. Further details about the experimental arrangement can be found in Ref. 8.

EXPERIMENTAL RESULTS

First we compare the time-integrated flame streaks of the freely-falling droplet streams of three distinctively different fuels, namely n-heptane, 1-azidohexane, and 1,6-diazidohexane. The heptane burning sequence is characterized by a blue flame and quiescent termination, without any indication of micro-explosion. For the azido fuel, the burning time is reduced while the burning is also terminated by a mild micro-explosion. The greatest change, however, occurs for the diazido fuel which exhibits a significantly reduced burning time, a larger flame dimension, and a violent termination behavior. It is clear that azido fuels, especially the diazides, require much less time for complete droplet gasification.

The enhanced gasification rates of the azido fuels can be quantified by plotting the square of the instantaneous droplet diameter D versus time

t. The results show that the d^2 -Law is obeyed for all three fuels when the burning is quiescent. The slopes then yield the burning rate constants

$$K = - \frac{dp^2}{dt}$$

The value of K for heptane is $1.0 \text{ mm}^2/\text{s}$, which is within the range of the accepted values in the literature, thereby validating the present methodology. It is, however, found that while the 1-azidoheptane exhibits only a moderate 20% increase in the burning rate, the burning rate constant of the 1,6-diazidoheptane is 2.6 times that of heptane.

Such increases can be further illustrated by comparing the K for straight chain molecules of the three families of alkanes, monoazides, and diazides with different carbon numbers. The significant increase in K for the diazides is impressive. In the extreme case of diazido-propane, $K = 6.7 \text{ mm}^2/\text{s}$ as compared to $K = 1.0 \text{ mm}^2/\text{s}$ for n-heptane.

We have also determined the normalized droplet size at micro-explosion, D_e/D_o , where D_e is the explosion droplet size and D_o the initial droplet size. It is seen from Table 1 that the diazides micro-explode earlier than the monoazides. We also note that while at micro-explosion the droplet is quite large, the droplet mass, which is proportional to $(D_e/D_o)^3$, is still small. An exception is 1,10-diazidodecane which explodes very early and therefore has the shortest burning time.

Because of the occurrence of micro-explosion, from the practical point of view a more useful indication of the burning rate of a fuel is not K but rather an effective burning rate constant defined as

$$K' = D_o^2/t_e$$

where t_e is the time to achieve micro-explosion. For fuels which do not exhibit micro-explosion, $K'=K$. Table 1 shows that K' is generally larger than K, hence further substantiating the potential of azides as fast burning fuels.

We have also determined the values of K for droplets undergoing pure vaporization. The results are summarized in Table 2. It is of significance to note that the gasification rates of diazides are again substantially higher than those of the alkanes.

DISCUSSIONS

Perhaps the most significant result of the present investigation is that droplets of organic diazides gasify rapidly and micro-explode early in the droplet lifetime. The actual mechanism responsible for the rapid gasification rate is unclear, although the following postulate can be made.

As is well established, the gasification rate of a droplet follows the relation

$$K \sim \ln(1+B)$$

where B is a transfer number. For the case of combustion,

$$B_c \sim Q/L$$

where Q is the heat of combustion and L the effective latent heat of gasification. Thus K increases with increasing B_c , although the logarithmic variation demands a substantial increase in B_c for a moderate increase in K , especially for $B_c > 1$ which is usually the case with combustion. Since K has been determined to be augmented by several hundred percent, the corresponding increase in B_c would have to be a few orders of magnitude. Such large increases in B_c cannot be realized by including the relatively small additional heat of decomposition in evaluating Q .

A large increase in B_c , however, can be achieved by assuming that decomposition of the azide occurs when the liquid azide is gasified. Implicit in this assumption is the requirement that at the gasification temperature the azide is stable in the liquid phase but unstable in the gaseous phase. Thus decomposition occurs instantly upon gasification, accompanied by the release of the decomposition heat. Since the heat of decomposition is of the same order as the heat of vaporization, the effective heat of gasification assumes a very small value. This then leads to a large B_c and the correspondingly large K . In the situation when the heat of decomposition exceeds the heat of gasification, the gasification process could become accelerative and is no longer described by the conventional droplet combustion results.

The above postulate is substantiated by the results on droplet vaporization. In this situation gas-phase combustion is absent such that the transfer number is

$$B_v \sim (T_\infty - T_g)/L.$$

Thus the only factor that can significantly influence B_v is L . As we have shown, in the case of vaporization, values of K for the diazides indeed also greatly exceed the corresponding values for the n -alkanes.

Finally, the result that the monoazides do not exhibit greatly increased K can be simply due to the possibility that, being more stable, decomposition does not occur during gasification.

CONCLUSIONS

The present experimental results have conclusively demonstrated that droplets of organic azides exhibit high rates of vaporization and burning as compared with the corresponding n -alkanes. The augmentation is especially significant for diazides, which show several hundred percent increases in the gasification rate. The azido droplets also micro-explode, with the diazides micro-exploding earlier in the droplet lifetime. These phenomena could be sensitive to the molecular structure in that branching of the base molecule seems to have a suppressive effect while presence of the OH group seems to enhance them.

It is also postulated that the strong response of the diazides could be due to the decomposition upon gasification. This possibility is currently being investigated both experimentally and theoretically.

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Table 1: A Comparison of Burning Rate Constants, K, Effective Burning Rate Constants, K', and Relative Micro-Explosion Diameters, D_e/D_0 , for Several Monoazides and Diazides.

Base Compound	Mono-Azides			Di-Azides		
	K(mm ² /s)	K'(mm ² /s)	D_e/D_0	K(mm ² /s)	K'(mm ² /s)	D_e/D_0
Propane	-	-	-	6.70	9.04	0.48
Butane	1.65	1.84	0.37	4.48	5.11	0.45
Pentane	1.30	1.40	0.34	3.30	3.96	0.43
Hexane	1.18	1.22	0.23	2.63	3.17	0.46
Heptane	1.15	-	-	2.06	3.19	0.67
Octane	1.10	1.50	-	-	-	-
Nonane	0.86	-	-	-	-	-
Decane	0.82	0.94	0.25	1.70	5.26	0.86

Table 2: A Comparison of Vaporization Rate Constant, K_v , for Several Monoazides and Diazides.

Base Compound	Alkanes		Mono-Azides		Di-Azides	
	Boiling Point(°C)	K (mm / ² s)	Boiling Point(°C)	K_v (mm / ² s)	Boiling Point(°C)	K_v (mm / ² s)
Propane	-42.1	-	-	-	180	-
Butane	- 0.5	-	109	-	-	-
Pentane	36.1	-	132	0.88	232	1.82
Hexane	69.0	-	156	0.78	242	1.58
Heptane	98.4	0.75	178	0.73	248	-
Octane	125.7	0.72	195	0.71	-	-
Nonane	150.8	0.65	206	0.63	-	-
Decane	174.1	0.54	-	-	295	-

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